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# Dynamics of Valence Fluctuations at Low Temperatures

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CITATION:

Kuramoto, Y.. Dynamics of Valence Fluctuations at Low Temperatures.  
物性研究 1982, 37(5): 92-93

ISSUE DATE:

1982-02-20

URL:

<http://hdl.handle.net/2433/90461>

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## §1. Introduction

Neutron scattering is a powerful method to probe the dynamics of magnetic moments in intermediate-valence (IV) compounds. Experimental results<sup>1)</sup> show that the dynamical magnetic susceptibility is nearly independent of the wave number and is of the form  $\chi(\omega) = \chi(0)\Gamma_M(-i\omega + \Gamma_M)^{-1}$ . In intermetallic IV compounds such as CePd<sub>3</sub>, CeSn<sub>3</sub>, YbCu<sub>2</sub>Si<sub>2</sub>, YbCuAl and so on the magnetic relaxation rate  $\Gamma_M(T)$  hardly depends on temperature  $T$  and is very large ( $\sim 10$  meV). We have already explained these features theoretically in the high temperature regime<sup>2)</sup>.

In these intermetallic compounds, resistivity decreases with decreasing temperatures below  $T \sim 100$  K in accordance with the metallic ground state<sup>1)</sup>. On the other hand, resistivity in TmSe shows a rapid increase with decreasing temperatures below  $T \sim 100$  K<sup>3)</sup>. Thus the ground state of TmSe is not metallic. The  $\Gamma_M(T)$  in TmSe does not depend on  $T$  above  $T > 100$  K as in intermetallic compounds but becomes proportional to  $T$  below  $T < 100$  K<sup>1)</sup>. A natural question which arises here is the following: How does  $\Gamma_M(T)$  in Sm compounds, for example, behave as a function of temperature where the ground state is not metallic? Examples are SmS under pressure ( $> 6.5$  kbar) and SmB<sub>6</sub> where resistivity increases with decreasing temperatures below  $T \sim 50$  K<sup>1)</sup>. Neutron scattering for Sm compounds has not yet been performed because a large capture cross section of Sm makes the experiment very difficult.

The purpose of our theoretical study is to elucidate whether the metallic ground state has some relevance to the constancy of  $\Gamma_M(T)$ . In other words, we want to settle the question whether TmSe is an exception concerning the behavior  $\Gamma_M(T) \sim k_B T$  at low temperatures. We have combined the Brillouin-Wigner perturbation theory and the renormalization-group treatment to solve the problem.

## §2. Model and a Renormalization-Group Analysis

In the first step we simplify the actual 4f configurations to those without orbital degeneracies. This model cannot deal with IV Tm compounds where both Tm<sup>2+</sup> and Tm<sup>3+</sup> have non-zero magnetic moments, but can simulate other IV compounds which have singlet in one of two valencies. Our aim here is to study whether the single-orbital model can lead to a non-singlet ground state in the IV regime. If the ground state is not a singlet, the relaxation at low temperatures should be of Korringa type, i.e.,  $\Gamma_M(T) \propto T$ . If, on the other hand, the ground state is always a singlet, the observed behavior  $\Gamma_M(T) \sim k_B T$  in TmSe should be ascribed to the special feature of IV Tm ions with non-zero magnetic moments.

In SmB<sub>6</sub>, for example, the conduction electron is supplied by the valence fluctuation alone and the attraction due to the resultant 4f hole may be important. We account for this feature by adding the potential scattering term to the Anderson model<sup>4)</sup> with  $U = \infty$ . In addition, there is a ferromagnetic direct s-f exchange<sup>5)</sup> which may even be stronger than the virtual s-f exchange induced by hybridization. We neglect the inter-site interaction of 4f electrons and write the model as

$$H = H_{\text{Anderson}} + (n_c - \langle n_c \rangle) (G \sum_{\sigma} X_{\sigma\sigma} - I X_{00}) - J \vec{s}_f \cdot \vec{s}_c, \quad (1)$$

where  $n_c$  and  $\vec{s}_c$  are charge and spin of the conduction electron at the impurity site and  $X_{\alpha\beta} = |\alpha\rangle\langle\beta|$  deals with 4f configurations  $|0\rangle$ ,  $|\uparrow\rangle$  and  $|\downarrow\rangle$ .  $G$ ,  $I$  and  $J$  are positive constants.

If the 4f energy level  $\epsilon_f$  is sufficiently below the Fermi level to satisfy  $J > 2V^2/|\epsilon_f|$  where  $V$  is the s-f hybridization energy, we have a localized spin and the ground state is a doublet. It is clear that the ground state is a

singlet when  $\epsilon_f \rightarrow \infty$ . Thus our task is to examine whether it is possible to have a doublet-singlet crossover in the IV regime.

We have compared the ground state energies of the singlet and the doublet using the Brillouin-Wigner perturbation theory and the cut-off scaling technique<sup>6)</sup>. The ground state energy  $E$  of the singlet is determined by the equation

$$E = \Sigma_S(E) = -2V^2\rho_c \int_0^{x_c} dl \frac{\exp[2\rho_c(G+I)]}{(1+J\rho_c l)^{3/2}}, \quad (2)$$

$$x_c = -\ln(\alpha|E|\rho_c)$$

where  $\rho_c$  is the density of states of the conduction band and  $\alpha$  is a numerical constant of the order of unity. Equation (2) reproduces the results by Keiter=Kimball<sup>7)</sup>, Inagaki<sup>8)</sup>, Ramakrishnan<sup>9)</sup> and others if we put  $G=I=J=0$ . For the doublet we should replace  $2V^2\rho_c$  by  $V^2\rho_c$ . In addition to the self-energy in (2) we have other self-energies from potential and exchange scatterings. They are insensitive to the energy  $E$  and irrelevant to the infrared effects we are interested in. It is found from (2) that the potential scattering enormously stabilizes the singlet, overwhelming the opposing action by  $J$ . Thus we have seen that the ground state of the model (1) is always the singlet in the IV regime.

The difference  $2V^2\rho_c$  and  $V^2\rho_c$  comes from the number of available intermediate states in one process of valence fluctuation. We have generalized the model (1) to account for the Tm ions, and have found that the octet originating from  $Tm^{2+}$  is the ground state. The octet, however, is a mixture of bare  $Tm^{2+}$  and  $Tm^{3+}$  configurations and has an IV. In contrast to the singlet, the octet must obey the Korringa relaxation process at low temperatures.

### §3. Discussion

Our theoretical consequence is that the Korringa-type relaxation observed in TmSe should be ascribed to the special situation of the IV Tm ion and cannot be expected in IV Sm compounds. On the contrary,  $\Gamma_M(T)$  in IV Sm compounds, if measured, may increase with decreasing temperatures because of the potential scattering or the excitonic effects.

Finally we discuss the reason why the proportionality constant  $C$  in  $\Gamma_M(T) = Ck_B T$  of TmSe is nearly unity. To deal with the problem quantitatively we must set up a transport equation for 4f "statistical quasi-particles"<sup>7)</sup>. Without going into details we summarize the result qualitatively: In the Korringa relaxation process the octet has intermediate states originating from  $Tm^{3+}$ . The intermediate states are almost resonant, which means that the scattering of a conduction electron is near the unitarity limit. Thus we have the proportionality constant of the order of unity. Quantitative details will be published soon.

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